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(21)Application number : 09-034144 (71)Applicant : SUMITOMO CHEM CO LTD

(22)Date of filing : 18.02.1997 (72)Inventor : NIITOME SATOSHI
ICHIKAWA KOJI

(54) MANUFACTURE OF RESIST COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To enhance precision in feeding a novolak resin and a quinonediazido derivative photosensitive agent to prepare the resist composition and to elevate the dimensional precision of the resist pattern to be obtained from this composition.

SOLUTION: The photoresist composition is manufactured by preparing the organic solvent solution of the quinonediazido derivative photosensitive agent and mixing it with the novolak resin. An alkali-soluble low molecular weight phenol resin may be added to this composition and it is preferred to add to it in the form of an organic solvent solution and it is preferred to add the novolak resin in the form of an organic solvent solution.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the resist constituent which is the approach
of manufacturing the resist constituent which comes to dissolve novolak resin and a
quinone diazide system sensitization agent in a solvent, prepares this quinone diazide
system sensitization agent in the form of the solution of an organic solvent, and is
characterized by mixing this with novolak resin.

[Claim 2] The approach according to claim 1 of this resist constituent containing the
low-molecular-weight phenol system additive of alkali fusibility further, and also
preparing this phenol system additive in the form of the solution of an organic solvent,

and mixing with other components.

[Claim 3] The approach according to claim 1 or 2 of also preparing this novolak resin in the form of the solution of an organic solvent.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the positive type photoresist constituent mainly used for micro processing of the semi-conductor by the near ultraviolet ray or far ultraviolet rays etc.

[0002]

[Description of the Prior Art] It is well-known to form into a quinone diazide sulfonate the compound which has a phenolic hydroxyl group generally, to form the resist film from the resist constituent which contains the ester as a sensitization agent, and to use for micro processing of a semi-conductor. namely, the constituent containing the sensitization agent which has a quinone diazide radical, and novolak resin -- a 300-500nm optical exposure -- the quinone diazide radical of a sensitization agent -- decomposing -- a carboxyl group -- being generated -- alkali -- the alkali from an insoluble condition -- this constituent is used as a positive resist using being in a meltable condition. Since this positive resist has the description of excelling in resolution compared with negative resist, it is used for manufacture of the various integrated circuits for semi-conductors.

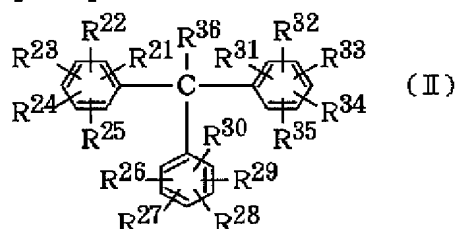
[0003]

[Problem(s) to be Solved by the Invention] The positive type photoresist is usually prepared by teaching the sensitization agent of the ingredient, especially a quinone diazide system in the form of fine particles. For this reason, the preparation precision (rate that the actual measurement is far apart to the desired value thru/or the certified value of a content of each ingredient in a resist) of an ingredient may become about $\pm 0.5\%$, and may produce dispersion in the dimension of a resist pattern etc. with that fluctuation. Then, solution of these problems, i.e., improvement in dimensional accuracy and improvement in preparation precision, was desired.

[0004] The purpose of this invention solves the trouble of said conventional technique, raises the raw material preparation precision of a positive type photoresist, raises dimensional accuracy by this, and is to manufacture the resist constituent suitable for

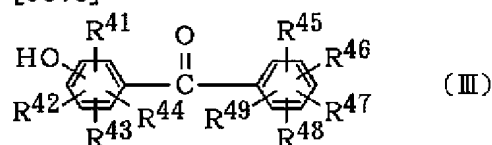
R2, R3, R4, R5, R6, R7, and R8, R9 In one of R10, the remainder a hydroxyl group and mutually-independent Hydrogen, a hydroxyl group, a halogen, alkyl, cycloalkyl, the alkenyl, Aryl, an aralkyl, alkoxy ** amino, monoalkylamino, Dialkylamino, alkyl carbonylamino, alkyl carbamoyl, Aryl carbamoyl, alkyl sulfamoyl, aryl sulfamoyl, Carboxyl, cyano ** nitroglycerine, the formyl, alkyl carbonyl, alkoxy carbonyl, Aryloxy carbonyl or alkylcarbonyloxy is expressed. R15, R16, R17, and R18 express hydrogen, a hydroxyl group, alkyl, cycloalkyl, the alkenyl, aryl, an aralkyl, or ARUKOKISHI mutually-independent.;

[0011]



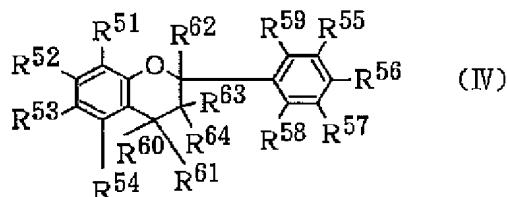
[0012] In a formula and 1 of R21, R22, R23, R24, R25, R26, R27, R28, R29, R30, R31, R32, R33, R34, and R35 a hydroxyl group The remainder mutually-independent Hydrogen, a hydroxyl group, a halogen, alkyl, cycloalkyl, The alkenyl, aryl, an aralkyl, alkoxy ** amino, monoalkylamino, Dialkylamino, alkyl carbonylamino, alkyl carbamoyl, Aryl carbamoyl, alkyl sulfamoyl, aryl sulfamoyl, Carboxyl, cyano ** nitroglycerine, the formyl, alkyl carbonyl, alkoxy carbonyl, Expressing aryloxy carbonyl or alkylcarbonyloxy, R36 expresses hydrogen, a hydroxyl group, alkyl, cycloalkyl, the alkenyl, aryl, an aralkyl, or ARUKOKISHI.;

[0013]



[0014] R41, R42, R43, R44, R45, R46, R47, R48, and R49 among a formula mutually-independent hydrogen, a hydroxyl group, a halogen, alkyl, cycloalkyl, the alkenyl, Aryl, an aralkyl, alkoxy ** amino, monoalkylamino, Dialkylamino, alkyl carbonylamino, alkyl carbamoyl, Aryl carbamoyl, alkyl sulfamoyl, aryl sulfamoyl, carboxyl Cyano ** nitroglycerine, the formyl, alkyl carbonyl, alkoxy carbonyl, aryloxy carbonyl, or alkylcarbonyloxy is expressed.;

[0015]



[0016] In a formula and 2 of R51, R52, R53, R54, R55, R56, and R57 a hydroxyl group The remainder mutually-independent Hydrogen, a hydroxyl group, a halogen, alkyl, cycloalkyl, The alkenyl, aryl, an aralkyl, alkoxy ** amino, monoalkylamino, Dialkylamino, alkyl carbonylamino, alkyl carbamoyl, Aryl carbamoyl, alkyl sulfamoyl, aryl sulfamoyl, Carboxyl, cyano ** nitroglycerine Formyl, alkyl carbonyl, Alkoxy carbonyl, aryloxy carbonyl, or alkylcarbonyloxy is expressed. Either R58 or R59 express a hydroxyl group, and another side expresses hydrogen, a hydroxyl group, or the alkyl of carbon numbers 1-4. Either R60 or R61 Alkyl, the alkenyl, cycloalkyl, or aryl is expressed. Another side of R60 and R61, R62, R63, and R64 mutually-independent Hydrogen, alkyl, cycloalkyl, The alkenyl, aryl, an aralkyl, alkoxy ** amino, monoalkylamino, Dialkylamino, alkyl carbonylamino, alkyl carbamoyl, Aryl carbamoyl, alkyl sulfamoyl, aryl sulfamoyl, [whether carboxyl, cyano ** nitroglycerine, alkyl carbonyl, alkoxy carbonyl, aryloxy carbonyl, or alkylcarbonyloxy is expressed and] Or R60 and R61 become together, and R62 and R63 become together, and the cycloalkane ring of carbon numbers 5-8 is formed with the carbon atom which each combines.

[0017] In the above-mentioned formula (I) - (IV) a halogen Alkyl as which it can be a fluorine, chlorine, a bromine, iodine, etc., and a carbon number is not specified (alkyl carbonyl etc.) It reaches including the case where alkyl combines with the radical of further others. Alkoxy (alkoxy carbonyl etc. includes the case where it combines with alkoxy ** and also other radicals) one It can be about one to ten carbon number, and cycloalkyl can be about five to eight carbon number, and the alkenyl can be about two to ten carbon number. Aryl (aryl carbamoyl etc. includes the case where aryl combines with the radical of further others) is phenyl or naphthyl typically, these may be permuted by the hydroxyl group or with a carbon number of about one to four alkyl, and aralkyls are benzyl, phenethyl, naphthyl methyl, naphthyl ethyl, etc. typically, and these rings may also be permuted by the hydroxyl group or with a carbon number of about one to four alkyl.

[0018] As a compound contained in a formula (I), the following is mentioned, for example.

[0019] 4-(2, 3, 4-trihydroxy benzyl) phenol, 2, and 5- or 2, a 6-dimethyl-4-(2, 3,

4-trihydroxy benzyl) phenol, 2, 3, and 5- or 2 and 3, a 6-trimethyl-4-(2, 3, 4-trihydroxy benzyl) phenol, 4- or 3-[1-(2, 3, 4-trihydroxy phenyl)-1-methylethyl] phenol, 4- or 3-[1-(2, 4-dihydroxy phenyl)-1-methylethyl] phenol, 4- or 3-[1-(2, 4-dihydroxy-3-methylphenyl)-1-methylethyl] phenol, 4-[1-(2, 4-dihydroxy phenyl)-1-methylethyl] resorcinol, 4-[1-(2, 3, 4-trihydroxy phenyl)-1-methylethyl] pyrogallol, 4-[1-(2, 4-dihydroxy-5-t-butylphenyl)-1-methylethyl] phenol, [0020] 2, 6-bis(2-hydroxy-5-methylbenzyl)-4-methyl phenol, 2, 6-bis(4-hydroxy - 3 and 5- or -2, 5-dimethylbenzyl)-4-methyl phenol, 2, 6-bis(2-hydroxy - 3, 5-dimethylbenzyl)-4-methyl phenol, 2, 6-bis(2, 4-dihydroxy benzyl)-4-methyl phenol, 2, 6-bis(2, 3, 4-trihydroxy benzyl)-4-methyl phenol, 1, 3-dihydroxy -4, 6-bis[1-(4- or 3-hydroxyphenyl)-1-methylethyl] benzene, 1, the 3-dihydroxy-2-methyl -4, 6-bis[1-(4- or 3-hydroxyphenyl)-1-methylethyl] benzene, [0021] 4,4'-methylenebis [2-(4-hydroxybenzyl)-3 and 6-dimethylphenol], 4,4'-methylenebis [2-(4-hydroxy - 2 and 5- or -3, 5-dimethylbenzyl)-3 and 6-dimethylphenol], 4,4'-methylenebis [2-(2-hydroxy-5-methylbenzyl)-3 and 6-dimethylphenol], 2,2'-methylene bis [6-(4-hydroxy-3-methylbenzyl)-4-methyl phenol], 4,4'-methylenebis [2-(4-hydroxy-3- or -2-methylbenzyl)-3 and 6-dimethylphenol], 4,4'-methylenebis [2-(2, 4-dihydroxy benzyl)-3 and 6-dimethylphenol], 4,4'-methylenebis [2-(4-hydroxy-3- or -2-methylbenzyl)-6-methyl phenol], 4,4'-methylenebis [2-(4-hydroxybenzyl)-6-methyl phenol], 4,4'-methylenebis [2-(2-hydroxy-5-methylbenzyl)-6-methyl phenol], 4,4'-methylenebis [2-(4-hydroxy - 2 and 5- or -3, 5-dimethylbenzyl)-6-methyl phenol], 1-[1 and 1-bis(4-hydroxyphenyl) ethyl]-4-[1-(4-hydroxyphenyl)-1-methylethyl] benzene, [0022] 2 and 4-bis[2-hydroxy-3-(4-hydroxy - 2, 3, 6-trimethyl benzyl)-5-methylbenzyl] - 3, 5, and a 6-trimethyl phenol - 2, 6-screw [4-hydroxy-3-(4-hydroxy-3- or -2-methylbenzyl)-2 and 5-dimethylbenzyl]-4-methyl phenol, 2, 6-screw [4-hydroxy-3-(4-hydroxy - 2, 6-dimethylbenzyl)-2 and 5-dimethylbenzyl]-4-methyl phenol, 2, 6-screw [4-hydroxy-3-(2-hydroxy-5-methylbenzyl)-2 and 5-dimethylbenzyl]-4-methyl phenol, 2, 6-screw [4-hydroxy-3-(2-hydroxybenzyl)-2 and 5-dimethylbenzyl]-4-methyl phenol, 2, 6-screw [4-hydroxy-3-(2-hydroxy - 4, 5-dimethylbenzyl)-2 and 5-dimethylbenzyl]-4-methyl phenol, 1, 4-bis[1-(4-hydroxy-3-(4-hydroxybenzyl)-5-methylphenyl)-1-methylethyl] benzene, 1, 4-bis[1-(4-hydroxy-3-(2-hydroxy-5-methylbenzyl) phenyl)-1-methylethyl] benzene, 4,4'-methylenebis [2-(4-hydroxy-3-(2, 4-dihydroxy benzyl)-5-methylbenzyl)-3 and 6-dimethylphenol] etc.

[0023] As a compound contained in a formula (II), the following is mentioned, for

example.

[0024] 4, 4', a 4''- trihydroxy triphenylmethane color, 3, 4', 4''-trihydroxy triphenylmethane color, 3''4, 4', 4''-tetra-hydroxy - 3, 3', 5, and 5'-tetramethyl triphenylmethane color, 2'' A 3''4, 4', 4''-pentahydroxy -3, 3', 5, and 5'-tetramethyl triphenylmethane color, 2'' A 4 and 4'-trihydroxy -2, 2', 5, and 5'-tetramethyl triphenylmethane color, A 2, 2', 2''-trihydroxy -4, 4', 5, and 5'-tetramethyl triphenylmethane color, 5, 5'-G t-butyl-3'', 4, 4', and 4'' - tetra--- a hydroxy-2 and 2'-dimethyl triphenylmethane color --- 5, 5'-G t-butyl-3'', 4, 4', and 4'' - tetra--- a hydroxy-2 and 2'-dimethoxy triphenylmethane color --- 5 and 5'-dicyclohexyl-3''4, 4', 4''-tetra-hydroxy - 2 and 2'-dimethyl triphenylmethane color, 5 and 5'-diisopropyl-3''4, 4', 4''-tetra-hydroxy - 2 and 2'-dimethyl triphenylmethane color, 5 and 5'-dicyclohexyl-3''4, 4', 4''-tetra-hydroxy - 2 and 2'-dimethoxy triphenylmethane color, 5 and 5'-diisopropyl-3''4, 4', 4''-tetra-hydroxy - 2 and 2'-dimethoxy triphenylmethane color, 5 and 5'-dicyclohexyl-2''4, 4', 5''-tetra-hydroxy - 2 and 2'-dimethyl triphenylmethane color, 5 and 5'-diisopropyl-2''4, 4', 5''-tetra-hydroxy - 2 and 2'-dimethyl triphenylmethane color, 5 and 5'-dicyclohexyl-2''4, 4', 5''-tetra-hydroxy - 2 and 2'-dimethoxy triphenylmethane color, 5 and 5'-diisopropyl-2''4, 4', 5''-tetra-hydroxy - 2 and 2'-dimethoxy triphenylmethane color, 2'' A 4 and 4'-, 3''4 and 4'- or 4, 4', 4''-trihydroxy -3, 3', 5, and 5'-tetramethyl triphenylmethane color, 4, 4', 4''-trihydroxy - 3'' - methoxy -3, 3', 5, and 5'-tetramethyl triphenylmethane color, 5 and 5'-dicyclohexyl - 2'' 4 and 4'-trihydroxy -2, a 2'-dimethyl triphenylmethane color, 5 and 5' -- a - diisopropyl-2''4 and 4'-trihydroxy -2, 2'-dimethyl triphenylmethane color, 4, 4', 4''-trihydroxy-3-methoxy triphenylmethane color etc.

[0025] Formula (III) As a compound contained, the following is mentioned, for example.

[0026] 2, 4-dihydroxy benzophenone, 2 and 3, 4-trihydroxy benzophenone, 2, 2', 3-trihydroxy benzophenone, 2, 2', 4-trihydroxy benzophenone, 2, 2', 5-trihydroxy benzophenone, 2 and 3, a 3'-trihydroxy benzophenone, 2, 3, a 4'-trihydroxy benzophenone, 2, 3', 4-trihydroxy benzophenone, 2, 3', 5-trihydroxy benzophenone, 2 and 4, a 4'-trihydroxy benzophenone, 2, 4', 5-trihydroxy benzophenone, 2', 3, 4-trihydroxy benzophenone, 3, 3', 4-trihydroxy benzophenone, 3 and 4, a 4'-trihydroxy benzophenone, A 2, 4, and 4'-trihydroxy-3-methyl benzophenone, 2 and 3, 3', and 4'-tetra-hydroxy benzophenone, A 2, 3, 4, and 4'-tetra-hydroxy benzophenone, 2, 2', 4, and 4'-tetra-hydroxy benzophenone, 2, 2', 3, a 4-tetra-hydroxy benzophenone, 2, 2', 3, a 4'-tetra-hydroxy benzophenone, A 2, 2', 5, and 5'-tetra-hydroxy benzophenone, 2, 3', 4', a 5-tetra-hydroxy benzophenone, 2, 3', 5, and 5'-tetra-hydroxy benzophenone, 2,

2', 4, and 4'-tetra-hydroxy - 3 and 3'-dimethylbenzo phenon, 2, 2', 3 and 4, a 4'-pentahydroxy benzophenone, 2, 2', 3 and 4, a 5'-pentahydroxy benzophenone, A 2, 2', 3, 3', 4-pentahydroxy benzophenone, 2 and 3, 3', 4, 5'-pentahydroxy benzophenone, 2 and 3, 3', 4, 4', and 5'-hexa hydroxy benzophenone, 2, 2', 3, 3', 4, a 5'-hexa hydroxy benzophenone, etc.

[0027] As a compound contained in a formula (IV), the following is mentioned, for example.

[0028] 2, 4, and 4-trimethyl -2', 4', 7-trihydroxy flavan, 2, 4, and 4-trimethyl -2', 3', 4', 7, 8-pentahydroxy flavan, 2, 3', 4 and 4, 8-pentamethyl - 2', 4', 7-trihydroxy flavan, 4-(1', 2', 3', 4', 4'a, and 9'a-hexahydro - cyclohexane -1 and 6'-hydroxy SUPIRO [9'-xanthene]-4'a-IRU) resorcinol, 4-(1', 2', 3', 4', 4'a, and 9'a-hexahydro-6'-hydroxy - cyclohexane -1 and 5'-methyl SUPIRO [9'-xanthene]-4'a-IRU)-2-methyl resorcinol, 4-(one -- ' -- two -- ' -- three -- ' -- three -- ' -- a -- nine -- ' -- nine -- ' -- a -- hexahydro - six -- ' - hydroxy ones -- SUPIRO -- [-- cyclopentane - one -- nine -- ' - cyclo -- PENTA -- [-- b --] -- chromene --] - three -- ' -- a - IRU) resorcinol etc.

[0029] The compound which has such a phenolic hydroxyl group is esterified by the condensation reaction with quinone diazide sulfonyl halide, and serves as a sensitization agent. The quinone diazide sulfonyl halide used here is usually o-quinone diazide sulfonyl halide, for example, 1 and 2-naphthoquinonediazide-4- or -5-sulfonyl halide, 1, and 2-benzoquinone diazido-4-sulfonyl halide etc. is mentioned.

[0030] Generally this condensation reaction is performed in an organic solvent. As an organic solvent to be used, ether like a tetrahydrofuran or dioxane for example, The solvent with which it mixes with water, such as amides like N.N-dimethylformamide, and sulfoxides like dimethyl sulfoxide Or the aliphatic hydrocarbon like n-hexane or n-heptane and the alicyclic hydrocarbon like a cyclohexane or a cyclopentane, The aromatic hydrocarbon like toluene or a xylene, and the halogenated aliphatic hydrocarbon like dichloromethane or chloroform The halogenated-aromatics hydrocarbons like a chlorobenzene or a dichlorobenzene Ethyl acetate, butyl acetate, the ester like amyl acetate, methyl isobutyl ketone, The ketones like 2-heptanone, ethylene glycol monomethyl ether acetate and ethylene glycol monoethyl ether acetate, Water, such as glycol ether ester like propylene-glycol-monomethyl-ether acetate and propylene glycol monoethyl ether acetate, and the solvent to separate are mentioned. These reaction solvents are independent, respectively, or two or more sorts can be mixed and they can be used. Moreover, this condensation reaction is performed under existence of a dehydrohalogenation agent. As a dehydrohalogenation

agent, an inorganic base like the fatty amines like triethylamine, annular amines like a pyridine, and a sodium hydrogencarbonate etc. is used, for example. After reaction termination, an acid, for example, an acetic acid etc., is added and a superfluous dehydrohalogenation agent is usually neutralized.

[0031] In this invention, a quinone diazide system sensitization agent is prepared in the form of the solution of an organic solvent, and it mixes with novolak resin in the condition. For that purpose, the approach of acquiring as a solution of the organic solvent which added the quinone diazide system sensitization agent by next etc. is employable by performing the condensation reaction of the compound and quinone diazide sulfonyl halide which have the above-mentioned phenolic hydroxyl group in an organic solvent, removing the salt of the dehydrohalogenation agent generated by the reaction and subsequent neutralization, adding another organic solvent and carrying out solvent exchange after the approach of obtaining a quinone diazide system sensitization agent as a solution of the organic solvent concerned, and a condensation reaction.

[0032] Moreover, before mixing with novolak resin, as for the organic solvent solution of this quinone diazide system sensitization agent, it is desirable to remove a part for a metal, halogen ion, etc. For that purpose, it is desirable to use a quinone diazide system sensitization agent as water and the organic solvent solution to separate, and to rinse it. Rinsing can mix the organic solvent solution of a quinone diazide system sensitization agent with sufficient quantity of water, and can be performed by separating liquids after stirring. As occasion demands, rinsing using a suitable quantity of water is also repeatable two or more times. When the condensation reaction of the compound and quinone diazide sulfonyl halide which have a phenolic hydroxyl group is performed in water and the organic solvent to separate, rinsing is performed by filtration etc. removing the salt of a dehydrohalogenation agent after neutralization, and subsequently adding and stirring water. Moreover, the approach of rinsing, while extracting a quinone diazide system sensitization agent and carrying out solvent exchange into this water and the organic solvent to separate is employable by filtration etc. removing the salt of a dehydrohalogenation agent after neutralization, and adding water, the organic solvent to separate, and water subsequently, stirring, and separating liquids, when the condensation reaction of the compound and quinone diazide sulfonyl halide which have a phenolic hydroxyl group is performed in the organic solvent with which it mixes with water.

[0033] As for the organic solvent which melts a quinone diazide system sensitization agent, it is desirable that they are the thing used as the solvent of a resist constituent,

for example, water and the ketones to separate, and glycol ether ester. Although the organic solvent solution of a quinone diazide system sensitization agent is obtained by rinsing and liquid separation, condensing generally is desirable, in order to remove after that the moisture contained in a solution, and in order to consider as concentration required to manufacture a resist constituent.

[0034] The novolak resin which is another component of a resist constituent is usually obtained by carrying out condensation of a phenol system compound and the aldehyde under existence of an acid catalyst. As a phenol system compound used as the raw material of novolak resin, o-, m- or p-cresol, 2, 5-, 3, 5- or 3, 4-xylenol, 2 and 3, a 5-trimethyl phenol, 2-t-butyl-5-methyl phenol, t-butyl hydroquinone, etc. are mentioned, for example. Moreover, the aromatic aldehyde like formaldehyde, an acetaldehyde, the aliphatic series aldehydes like glyoxal and a benzaldehyde, and salicylaldehyde as an aldehyde which is another raw material of novolak resin is mentioned.

[0035] Novolak resin is obtained by carrying out condensation of one sort of these phenols system compound or two sorts or more, one sort of an aldehyde, or the two sorts or more under existence of an acid catalyst. As an acid catalyst, a hydrochloric acid, a sulfuric acid, an inorganic acid like a phosphoric acid, oxalic acid, an acetic acid, an organic acid like p-toluenesulfonic acid, a divalent metal salt like zinc acetate, etc. are used. A condensation reaction can be performed according to a conventional method, for example, is performed at the temperature of the range which is 60–120 degrees C for about 2 to 30 hours. Moreover, a reaction may be performed with bulk or you may carry out in a suitable solvent. As for the novolak resin obtained, it is desirable to operate judgment etc. and to make it the surface ratio of 900 or less component become 25% or less and 20 more% or less to a total pattern area except the pattern area of an unreacted phenol system compound in the pattern by the gel permeation chromatography (GPC) (for the detector of UV254nm to be used) with polystyrene conversion molecular weight.

[0036] It is desirable to also prepare this novolak resin in the form of the solution of an organic solvent, and to mix it with the organic solvent solution of the aforementioned quinone diazide system sensitization agent in this invention. Also as for the organic solvent which melts novolak resin, it is desirable that it is a thing used as the solvent of a resist constituent. When the above judgment actuation is performed to novolak resin, novolak resin can be obtained as a solution of the organic solvent of arbitration by operating solvent exchange by request after that.

[0037] In this invention, the polyhydric-phenol compound which has the

low-molecular-weight phenol system additive of alkali fusibility in a resist constituent, and has at least two phenolic hydroxyl groups in intramolecular with 900 or less molecular weight can be blended again. When blending such a low-molecular-weight phenol system additive, also as for this additive, it is desirable to mix with the quinone diazide system sensitization agent which prepared in the form of the solution of an organic solvent and was prepared in the form of the aforementioned novolak resin and an organic solvent solution. For example, the additive prepared in the solid form can be made into the form of a solution by dissolving in a suitable organic solvent. Also as for the organic solvent used here, it is desirable that it is a thing used as the solvent of a resist constituent.

[0038] After it has a suitable rate of drying and a solvent evaporates, as for the solvent of a resist constituent, what gives a uniform and smooth paint film is good. As such a solvent, the glycol ether ester like ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, and propylene-glycol-monomethyl-ether acetate, the ketones like a cyclohexanone or 2-heptanone, and the ester like n-amyl acetate are mentioned, for example. These solvents are independent, respectively, or two or more sorts can be mixed and they can be used. Moreover, little content of the organic solvent with which it mixes with water like ethyl lactate or gamma-butyrolactone can also be carried out if needed.

[0039] The quinone diazide system sensitization agent prepared in the form of the solution of an organic solvent will serve as a resist constituent novolak resin and by mixing with an additional solvent, the low-molecular-weight phenol system additive further used according to a request, if required. In this way, the prepared resist constituent can also carry out little content of other components, for example, a color, the resin other than novolak resin, etc. as an additive again if needed.

[0040] In the resist constituent manufactured by this invention, especially the presentation rate of each component can be a value which is not limited but is usually adopted in this field. Although the presentation rate changes with the class of quinone diazide system sensitization agent, the existence of a low-molecular-weight phenol system additive, etc., when novolak resin is 50 % of the weight or more, and a quinone diazide system sensitization agent is about 10 - 50% of the weight of the range and it uses a low-molecular-weight phenol system additive on the basis of the amount of total solids of a resist constituent, generally it is about 3 - 40 % of the weight.

[0041]

[Example] Next, although an example is given and this invention is explained still more concretely, this invention is not limited at all by these examples. The section in an

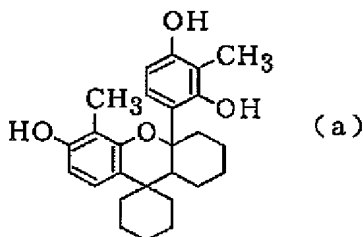
example and especially a concentration display are weight criteria unless it refuses.

[0042] The example of reference (manufacture of novolak resin)

Teaching the m-cresol 148.5 section, the p-cresol 121.5 section, the methyl-isobutyl-ketone 252 section, the 10% oxalic acid water-solution 37.0 section, and the 90% acetic-acid water-solution 84.8 section, and carrying out heating stirring with a 100-degree C oil bath, the formalin 129.5 section was dropped at the 4 opening flask over 40 minutes 37.0%, and it was made to react to it after that for further 15 hours. Next, rinsing dehydration was carried out and the methyl-isobutyl-ketone solution 466 section which contains novolak resin 42.3% was obtained. Polystyrene equivalent weight average molecular weight by GPC It was 4,300.

[0043] Liquids were put and separated, after having taught this solution 450 section to the bottom omission separable flask, adding the methyl-isobutyl-ketone 909.6 section and the n-heptane 996.1 section further and stirring for 30 minutes at 60 degrees C. To the lower layer mass obtained by liquid separation, the evaporator removed 380 *****, methyl isobutyl ketone, and n-heptane for 2-heptanone, and 2-heptanone solution of novolak resin was obtained to it. Polystyrene equivalent weight mean molecular weight by GPC It was 9,000 and the surface ratio of 900 or less range was 14% to a total pattern area in polystyrene conversion molecular weight.

[0044] The example 1 (manufacture of a sensitization agent solution) of preparation It is (Formula a) [0045] the bottom.



[0046] ***** 4- which it has 1', 2', 3', 4', and 4'a -- One mol of 9'a-hexahydro-6'-hydroxy-5'-methyl SUPIRO [cyclohexane -1 and 9'-xanthene]-4'a-IRU-2-methyl resorcinols, and two mols of 1 and 2-naphthoquinonediazide-5-sulfonyl chloride It is made to dissolve completely in 4.72l. of dioxanes, and 2.4 mols of triethylamines are dropped at the solution, and it was made to react until 1 and 2-naphthoquinonediazide-5-sulfonyl chloride was no longer detected. After reaction termination, 0.6 mols of acetic acids were added, it stirred for 1 hour, and, subsequently precipitate (salt of an amine) was filtered. 6l. of 2-heptanone and 3l. of ion exchange water were added and washed to filtrate, and

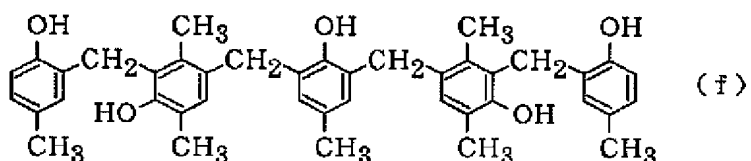
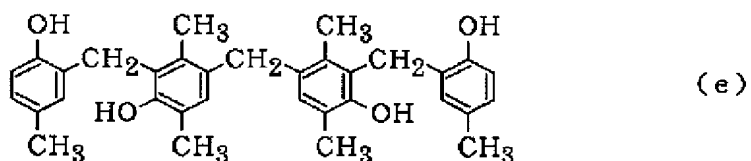
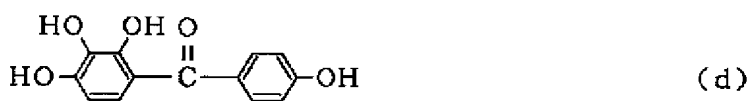
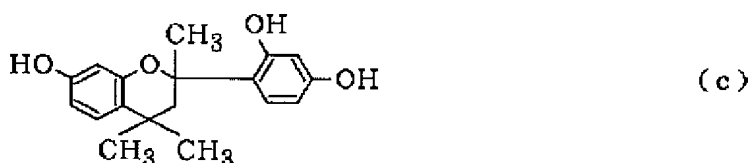
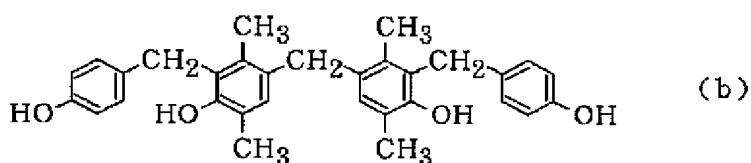
processing except a part for a metal or a chlorine ion was performed. 2-heptanone layer was taken out after liquid separation, it condensed until solid content became about 20%, and 2-heptanone solution of a sensitization agent was obtained.

[0047] The examples 2-6 (manufacture of another sensitization agent solution) of preparation

Formula used in the example 1 of preparation (a) 4,4'-methylenebis which replaces with a compound and has the structure of a bottom type, respectively

[2-(4-hydroxybenzyl)-3 and 6-dimethylphenol] (bottom type (b): example 2 of preparation), 2, 4, and 4'-trimethyl -2', 4', 7-trihydroxy flavan (bottom type (c) : example 3 of preparation), A 2, 3, 4, and 4'-tetra-hydroxy benzophenone (bottom type (d) : example 4 of preparation), 4,4'-methylenebis [2- (2-hydroxy-5-methylbenzyl) -3, 6-dimethylphenol] (bottom type (e) : example 5 of preparation) or 2, 6-screw [4-hydroxy-3-(2-hydroxy-5-methylbenzyl)-2 and 5-dimethylbenzyl]-4-methyl phenol (bottom type (f)) : Except having used the example 6 of preparation the said molar quantity every, the same actuation as the example 1 of preparation was performed, and 2-heptanone solution which contains each sensitization agent by concentration about 20% was obtained.

[0048]



[0049] The example 7 (manufacture of the sensitization agent solution by the option) of preparation

The same 4- as having used in the example 1 of preparation 1', 2', 3', 4', and 4'a --

One mol of 9'a-hexahydro-6'-hydroxy-5'-methyl SUPIRO [cyclohexane -1 and 9'-xanthene]-4'a-IRU-2-methyl resorcinols, and two mols of 1 and 2-naphthoquinonediazide-5-sulfonyl chloride It is made to dissolve completely in 4l. of 2-heptanone, and 2.4 mols of triethylamines are dropped at the solution, and it was made to react until 1 and 2-naphthoquinonediazide-5-sulfonyl chloride was no longer detected. After reaction termination, 0.6 mols of acetic acids were added, it stirred for 1 hour, and, subsequently precipitate (salt of an amine) was filtered. 3l. of ion exchange water was added and washed to filtrate, and processing except a part for a metal or a chlorine ion was performed. After liquid separation, 2-heptanone layer was condensed until solid content became about 20%, and 2-heptanone solution of the sensitization agent same with having been obtained in the example 1 of preparation was obtained.

[0050] The examples 8-12 (manufacture of another sensitization agent solution) of preparation

It replaces with the 4-(1', 2', 3', 4', 4'a, and 9'a-hexahydro-6'-hydroxy - cyclohexane -1 and 5'-methyl SUPIRO [9'-xanthene]-4'a-IRU)-2-methyl resorcinol used in the example 7 of preparation. The same 4,4'-methylenebis as having used in the examples 2-6 of preparation, respectively [2-(4-hydroxybenzyl)-3 and 6-dimethylphenol] (example 8 of preparation), 2, 4, and 4-trimethyl -2', 4', 7-trihydroxy flavan (example 9 of preparation), A 2, 3, 4, and 4'-tetra-hydroxy benzophenone (example 10 of preparation), 4,4'-methylenebis [2-(2-hydroxy-5-methylbenzyl)-3 and 6-dimethylphenol] (example 11 of preparation), 2 and 6-screw [4-hydroxy-3-(2-hydroxy-5-methylbenzyl)-2 and 5-dimethylbenzyl]-4-methyl phenol (example 12 of preparation) the said molar quantity every or except having used The same actuation as the example 7 of preparation was performed, and 2-heptanone solution which contains the sensitization agent same with having been obtained in the examples 2-6 of preparation, respectively by concentration about 20% was obtained.

[0051] The example 13 (comparison: manufacture of a fine-particles sensitization agent) of preparation

The same 4- as having used in the example 1 of preparation 1', 2', 3', 4', and 4'a — One mol of 9'a-hexahydro-6'-hydroxy-5'-methyl SUPIRO [cyclohexane -1 and 9'-xanthene]-4'a-IRU)-2-methyl resorcinols, and two mols of 1 and 2-naphthoquinonediazide-5-sulfonyl chloride It is made to dissolve completely in 4.72l. of dioxanes. 2.4 mols of triethylamines are dropped at the solution, and it was made to react until 1 and 2-naphthoquinonediazide-5-sulfonyl chloride was no longer detected. After reaction termination, 0.6 mols of acetic acids were added, it stirred for 1 hour, and, subsequently precipitate (salt of an amine) was filtered. Filtrate was fed into the acetic-acid water solution 1%, the sludge was filtered, ion exchange water often washed this filtration object, and processing except a part for a metal or a chlorine ion was performed. The sensitization agent of fine particles was obtained by drying this.

[0052] The examples 14-18 (comparison: manufacture of another fine-particles sensitization agent) of preparation

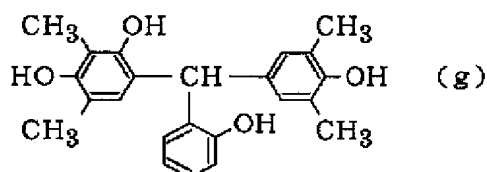
It replaces with the 4-(1', 2', 3', 4', 4'a, and 9'a-hexahydro-6'-hydroxy - cyclohexane -1 and 5'-methyl SUPIRO [9'-xanthene]-4'a-IRU)-2-methyl resorcinol used in the example 13 of preparation. having used in the examples 2-6 of preparation, respectively -- the same -- 4,4'-methylenebis [2-(4-hydroxybenzyl)-3 and 6-dimethylphenol] (example 14 of preparation) -- 2, 4, and 4-trimethyl -2', 4',

7-trihydroxy flavan (example 15 of preparation), A 2, 3, 4, and 4'-tetra-hydroxy benzophenone (example 16 of preparation), 4,4'-methylenebis [2-(2-hydroxy-5-methylbenzyl)-3 and 6-dimethylphenol] (example 17 of preparation), Or except having used 2 and 6-screw [4-hydroxy-3-(2-hydroxy-5-methylbenzyl)-2 and 5-dimethylbenzyl]-4-methyl phenol (example 18 of preparation) the said molar quantity every, the same actuation as the example 13 of preparation was performed, and each sensitization agent was obtained in the form of fine particles.

[0053] The example 19 (manufacture of a phenol system additive solution) of preparation

0.2 mols of p-toluenesulfonic acid were taught to the solution which contains 2.5 mols of 2 and 6-xlenols, and one mol of salichlaldehydes in methanol 400g Naka, and it stirred until salichlaldehyde was no longer detected. 200g of ion exchange water was added after reaction termination, and it filtered, after fully depositing a crystal. After carrying out the rinse of the filtration object in a methanol water solution 60%, it dissolved in 2-heptanone 500g, ion exchange water washed, and a part for a metal was removed. Next, the preparation of concentration and 2-heptanone was repeated, and it adjusted so that the concentration of a resultant might finally become 25%, so that water might become 0.1% or less. Thus, bottom type (g) 2-heptanone solution of 4 which has structure, 4'-(2-hydroxy benzylidene) G 2, and 6-xlenol was obtained.

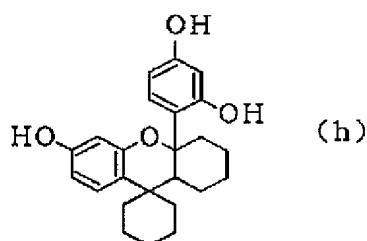
[0054]



[0055] The example 20 (manufacture of another phenol system additive solution) of preparation

Except having changed starting material into 1.2 mols of resorcinols, and one mol of cyclohexanones, the same actuation as the example 19 of preparation is performed, and it is a bottom type (h). 2-heptanone solution which contains 4-(1', 2', 3', 4', 4'a, and 9'a-hexahydro - cyclohexane -1 and 6'-hydroxy SUPIRO [9'-xanthene]-4'a-IRU) resorcinol which has structure 25% was obtained.

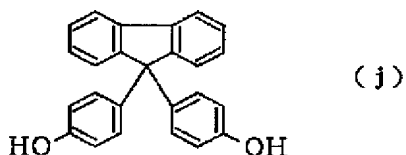
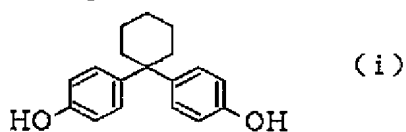
[0056]



[0057] The examples 21 and 22 (manufacture of another phenol system additive solution) of preparation

It is a bottom type, respectively. (i) or (j) Dissolving the 1 of marketing which has structure, 1-bis(4-hydroxyphenyl) cyclohexane (example 21 of preparation) or 9, and 9-bis(4-hydroxyphenyl) fluorene (example 22 of preparation) in 2-heptanone, the same actuation as the example 19 of preparation was performed after rinsing, and it obtained 2-heptanone solution which contains each compound 25%.

[0058]

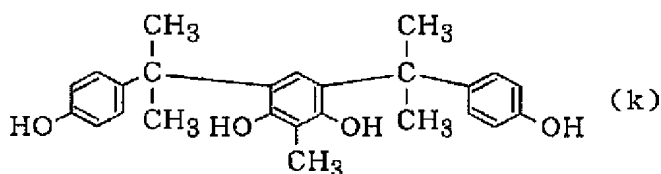


[0059] The example 23 (manufacture of another phenol system additive solution) of preparation

0.02 mols of hydrochloric-acid water solutions were thrown into the mixed liquor which contains 2.1 mols of p-isopropenyl phenols, and one mol of 2-methyl resorcinols in toluene 400g Naka 1%, and it stirred at 40 degrees C for 2 hours. After filtering the solid-state after reaction termination and carrying out a rinse with toluene, it dissolved in 2-heptanone. The same actuation as the example 19 of preparation is performed after rinsing, and it is a bottom type (k). 2-heptanone solution which contains 4 which has structure, and 6-screw

[1-(4-hydroxyphenyl)-1-methylethyl]-2-methyl resorcinol 25% was obtained.

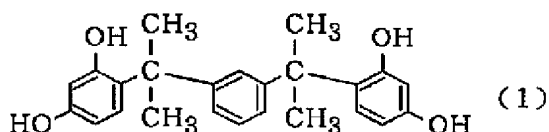
[0060]



[0061] The example 24 (manufacture of another phenol system additive solution) of preparation

The same actuation as the example 23 of preparation is performed except having changed starting material into 2.1 mols of resorcinols, and one mol (2-propanol) of 2 and 2'-m-phenylene screws. Bottom type (l) 2-heptanone solution which contains 1 which has structure, and 3-bis[1-(2, 4-dihydroxy phenyl)-1-methylethyl] benzene 25% was obtained.

[0062]



[0063] The example 25 (comparison: manufacture of a fine-particles phenol system additive) of preparation

0.2 mols of p-toluenesulfonic acid were taught to the solution which contains 2.5 mols of 2 and 6-xilenols, and one mol of salichlaldehydes in methanol 400g Naka, and it stirred until salichlaldehyde was no longer detected. 200g of ion exchange water was added after reaction termination, and it filtered, after fully depositing a crystal. After carrying out the rinse of the filtration object in a methanol water solution 60%, it dissolved in 200g of ethyl acetate, and toluene 500g mixed liquor, ion exchange water washed, and a part for a metal was removed. After concentration, toluene was added a distilled off part and the crystal was fully deposited until ethyl-acetate concentration became 5% or less, and it filtered. This filtration object is dried and it is said formula (g). 4 which has structure, 4'-(2-hydroxy benzyldiene) G 2, and 6-xilenol were obtained as fine particles.

[0064] The example 26 (comparison: manufacture of another fine-particles phenol system additive) of preparation

Except having changed starting material into 1.2 mols of resorcinols, and one mol of cyclohexanones, the same actuation as the example 25 of preparation was performed, and 4-(1', 2', 3', 4', 4'a, and 9'a-hexahydro - cyclohexane -1 and 6'-hydroxy SUPIRO [9'-xanthene]-4'a-IRU) resorcinol which has the structure of said formula (h) was

obtained as fine particles.

[0065] The example 27 (comparison: manufacture of another fine-particles phenol system additive) of preparation

0.02 mols of hydrochloric-acid water solutions were thrown into the mixed liquor which contains 2.1 mols of p-isopropenyl phenols, and one mol of 2-methyl resorcinols in toluene 400g Naka 1%, and it stirred at 40 degrees C for 2 hours. After filtering the solid-state after reaction termination and carrying out a rinse with toluene, it dissolved in 200g of ethyl acetate, and toluene 500g mixed liquor, ion exchange water washed, and a part for a metal was removed. After concentration, toluene was added a distilled off part and the crystal was fully deposited until ethyl-acetate concentration became 5% or less, and it filtered. This filtration object is dried and it is said formula (k). The 4 and 6-screw

[1-(4-hydroxyphenyl)-1-methylethyl]-2-methyl resorcinol which has structure was obtained as fine particles.

[0066] The example 28 (comparison: manufacture of another fine-particles phenol system additive) of preparation

Except having changed starting material into 2.1 mols of resorcinols, and one mol (2-propanol) of 2 and 2'-m-phenylene screws, the same actuation as the example 27 of preparation is performed, and it is said formula (l). 1 which has structure, and 3-bis[1-(2, 4-dihydroxy phenyl)-1-methylethyl] benzene were obtained as fine particles.

[0067] Said formula obtained in the example 5 of example preparation (e) The solution of the quinone diazide sulfonate of the 4,4'-methylenebis

[2-(2-hydroxy-5-methylbenzyl)-3 and 6-dimethylphenol] which has structure by solid content conversion The seven sections, Said formula obtained in the example 20 of preparation (h) The solution of 4-(1', 2', 3', 4', 4'a, and 9'a-hexahydro - cyclohexane -1 and 6'-hydroxy SUPIRO [9'-xanthene]-4'a-IRU) resorcinol which has structure by solid content conversion The 3.1 sections, Said formula obtained in the example 21 of preparation (i) The solution of 1 which has structure, and a 1-bis(4-hydroxyphenyl) cyclohexane by solid content conversion The 1.1 sections, And weight average molecular weight which taught 2-heptanone and was obtained in the example of reference after that The solution of the novolak resin of 9,000 was stirred by 10.13 ***** by solid content conversion. 2-heptanone was adjusted so that it might become the 60 sections in total. After equalization, precision filtration was carried out and the positive type photoresist was obtained.

[0068] The above actuation was repeated several times and two or more lot

manufacture of the same positive type photoresist was carried out fundamentally. The thing of each lot was applied to the silicon wafer, it exposed through the mask predetermined [after desiccation], negatives were developed with the alkali developer, and the positive type pattern was formed. Consequently, for the positive type pattern obtained from each lot, a dimension is 0.35×0.015 micrometers. It was settled in specification. Moreover, the preparation precision of a raw material was able to be suppressed within $\pm 0.15\%$ to desired value.

[0069] also when it combined with versatility using each component obtained by the examples 1–12 of preparation, and 19–24, the almost same result as the above-mentioned example was obtained, and the effectiveness of an improvement was accepted.

[0070] Said formula obtained in the example 17 of example preparation of a comparison (e) The quinone diazide sulfonate (fine particles) of the 4,4'-methylenebis [2-(2-hydroxy-5-methylbenzyl)-3 and 6-dimethylphenol] which has structure The seven sections, Said formula obtained in the example 26 of preparation (h) 4-(1', 2', 3', 4', 4'a, and 9'a-hexahydro - cyclohexane -1 and 6'-hydroxy SUPIRO

[9'-xanthene]-4'a-IRU) resorcinol (fine particles) which has structure The 3.1 sections, Said commercial formula (i) The 1.1 sections and 2-heptanone are taught for 1 which has structure, and a 1-bis(4-hydroxyphenyl) cyclohexane (fine particles). Weight average molecular weight obtained in the example of reference after that The solution of the novolak resin of 9,000 was stirred by 10.13 ***** by solid content conversion. 2-heptanone was adjusted so that it might become the 60 sections in total. After equalization, precision filtration was carried out and the positive type photoresist was obtained.

[0071] The above actuation was repeated several times and two or more lot manufacture of the same positive type photoresist was carried out fundamentally. The thing of each lot was applied to the silicon wafer, it exposed through the mask predetermined [after desiccation], negatives were developed with the alkali developer, and the positive type pattern was formed. Consequently, for the positive type pattern obtained from each lot, a dimension is 0.35×0.02 micrometers. It was distributed. Moreover, the preparation precision of a raw material was $\pm 0.5\%$ to desired value.

[0072]

[Effect of the Invention] According to this invention, the dimensional accuracy of the resist pattern which the preparation precision of the raw material of a positive type photoresist can be raised, and is formed can also be raised. Therefore, the approach

of this invention is useful to manufacture of the positive type photoresist as which precision is required, and especially formation of the resist pattern using it further.

[Translation done.]